

# PATENT ABSTRACTS OF JAPAN

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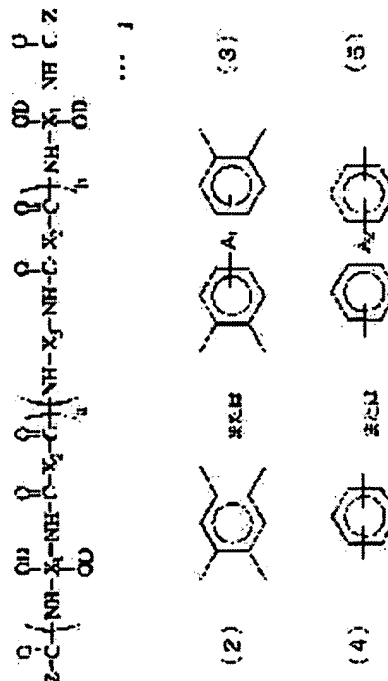
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## (54) PHOTSENSITIVE POLYAMIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a photosensitive resin composition which has high sensitivity, gives a pattern having high residual film rate and high contrast and is excellent in the resolution of a fine pattern and in the shape of a pattern, and a new photosensitive polyamide used for the composition.

SOLUTION: The photosensitive resin composition contains a photosensitive polyamide represented by formula (1) [wherein X1 is a group of formula (2) or formula (3) (wherein A1 is a single bond, O, C(CF<sub>3</sub>)<sub>2</sub>, CO or SO<sub>2</sub>); X2 is a group of formula (4) or formula (5) (wherein A2 is a single bond, O, C(CF<sub>3</sub>)<sub>2</sub>, CO or SO<sub>2</sub>); X3 is a divalent organic group; (a) and (b) are each a mol fraction, a+b=100 mol%, a=60.0 to 100 mol%, and b=0 to 40.0 mol%; D is a 1,2- naphthoquinonediazido-4-sulfonate residue, 1,2- naphthoquinonediazido-5-sulfonate residue, or H; and Z is an aliphatic, alicyclic or aromatic group having at least one alkenyl or alkynyl group].



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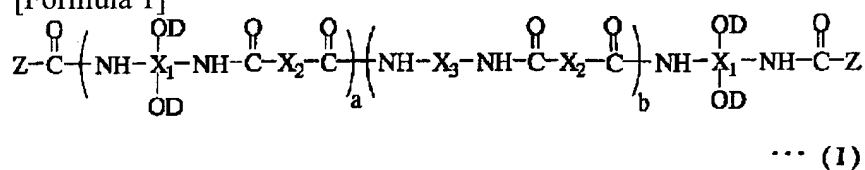
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## CLAIMS

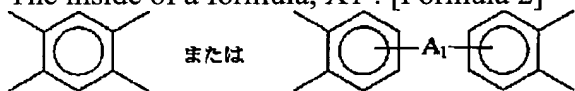
[Claim(s)]

[Claim 1] A photosensitive polyamide shown by the following general formula (I).

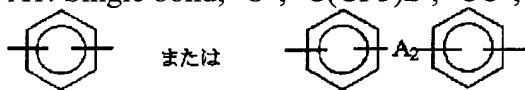
[Formula 1]



The inside of a formula, X1 : [Formula 2]



A1: Single bond, -O-, -C(CF<sub>3</sub>)<sub>2</sub>-, -CO-, or -SO<sub>2</sub>-X<sub>2</sub> : [Formula 3]



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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the photopolymer constituent containing a new photosensitivity polyamide and this new photosensitivity polyamide. Furthermore, it is related with the photopolymer constituent containing the new photosensitivity polyamide which can be preferably used for details at various uses, such as a surface-protection film of a semiconductor device, and an interlayer insulation film, and this new photosensitivity polyamide.

[0002]

[Description of the Prior Art] Conventionally, the polyimide resin it has polyimide resin, the outstanding thermal resistance, an electrical property, a mechanical characteristic, etc. as the surface-protection film of a semiconductor device and an interlayer insulation film is used. While the further high integration of a semiconductor device and enlargement progress in recent years, in order to attain thin-shape-izing of a closure resin package, and a miniaturization and to meet this demand, methods, such as LOC (lead-on chip) and a surface mount by the solder reflow, are adopted, and the polyimide resin which was excellent in micro-processing nature, a mechanical characteristic, thermal resistance, etc. more than the former has come to be needed. To these demands, by giving photosensitive ability to polyimide resin itself, the photosensitive polyimide resin which made formation of the detailed pattern by light easy is developed and put in practical use, and has been used widely. As development of such technology, the positive type photopolymer which research of the photopolymer of the positive type which can do development is made in the alkali aqueous solution, for example, becomes JP,1-46862,B, JP,8-269198,A, JP,64-6947,A, JP,3-20743,A, JP,9-321038,A, and JP,8-123034,A from poly benzo oxazole resin or poly benzo oxazole precursive resin, and a quinone diazide system sensitization agent is indicated recently. Moreover, in JP,3-87745,A, the photopolymer of one apparatus which made the quinone diazide system sensitization radical react to poly benzo oxazole precursor resin is indicated. These have the outstanding thermal resistance, an electrical property, and micro-processing nature, and have the possibility of not only a wafer coat use but the use as an interlayer insulation film.

[0003] However, since the solubility difference of the exposure section and the unexposed section was small, namely, was low contrast as compared with the general positive resist which consists of novolak resin and a quinone diazide system sensitization agent and the photopolymer constituent using these poly benzo oxazole resin was low sensitivity, it had a problem practically.

[0004]

[Problem(s) to be Solved by the Invention] This invention fulfills simultaneously the property currently demanded from these former, i.e., the pattern of a high remaining rate of membrane and high contrast can be obtained by high sensitivity, and it aims at offering the photopolymer constituent which was simultaneously excellent in the definition and the pattern configuration of a detailed pattern, and the new photosensitivity polyamide used for this photopolymer constituent.

[0005]

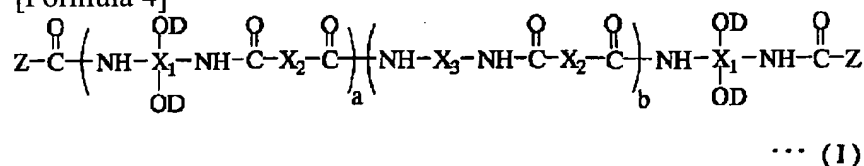
[Means for Solving the Problem] this invention persons accomplish a header and this invention for a

photopolymer constituent using a photosensitive polyamide which has specific principal chain structure, and is made to carry out the esterification reaction of the quinone diazide system sensitization radical to a polyamide which closed a part for an end by aliphatic series which has an alkenyl radical or at least one alkynyl group, alicyclic, or aromatic series radical, and is obtained fulfilling said property, as a result of performing research and examination wholeheartedly.

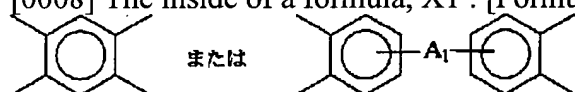
[0006] That is, this invention relates to a photosensitive polyamide shown by the following general formula (I).

[0007]

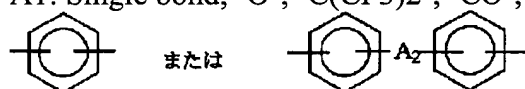
[Formula 4]



[0008] The inside of a formula, X1 : [Formula 5]



A1: Single bond, -O-, -C(CF<sub>3</sub>)<sub>2</sub>-, -CO-, or -SO<sub>2</sub>-X<sub>2</sub> : [Formula 6]



A2 : The organic radical a of single bond, -O-, -C(CF<sub>3</sub>)<sub>2</sub>-, -CO-, or -SO<sub>2</sub>-X<sub>3</sub>:2 \*\* and b:mole fraction are expressed. It is a+b= 100-mol %. a= 60.0-100-mol % and b=0-40.0 mol %D:1 and 2-naphthoquinonediazide-4-sulfonate residue, 1 and 2-naphthoquinonediazide-5-sulfonate residue or a hydrogen atom is expressed. 50% or less of all D is 1 and 2-naphthoquinonediazide-4-sulfonate residue or 1, and 2-naphthoquinonediazide-5-sulfonate residue, and the remainder is a hydrogen atom.

Z: They are the aliphatic series which has an alkenyl radical or at least one alkynyl group, alicyclic, or an aromatic series radical.

[0009] Moreover, this invention relates to the photopolymer constituent containing the photosensitive polyamide shown by the above-mentioned general formula (I).

[0010] Hereafter, this invention is further explained to details. The photosensitive polyimide of this invention is manufactured by the reaction of the polyamide (this may be hereafter called "polyamide before esterification") whose radical D in the above-mentioned general formula (I) is a hydrogen atom altogether, and 1, 2-naphthoquinonediazide-4-sulfonic acid, 1, and 2-naphthoquinonediazide-5-sulfonic acid or these acid halide. The polyamide before esterification can form into acid chloride the dicarboxylic acid which is a method given in JP,64-6947,A, JP,60-223824,A, JP,63-96162,A, etc. using a thionyl chloride etc., and can obtain it by dihydroxy diamine, the method of making it condense, and the method of condensing dicarboxylic acid and dihydroxy diamine with condensing agents, such as dicyclohexylcarbodiimide. At this time, for the object, such as raising the conservation stability of a constituent, closure reforming of the chain end of a polyamide can be carried out using various kinds of intramolecular cyclic anhydrides or acid chloride, by using the radical in a general formula (I) Z. Becoming, it is high sensitivity and the pattern of a high remaining rate of membrane can be obtained in that case. If this polyamide is heated at about 300-400 degrees C, a dehydration ring closure will be carried out and it will change to heat resistant resin called the poly benzo oxazole.

[0011] In this invention, as dicarboxylic acid used for the polyamide manufacture before esterification For example, phthalic-acid, isophthalic acid, terephthalic-acid, 3, and 3'-diphenyl dicarboxylic acid, 3, -diphenyl dicarboxylic acid, and 4 '4, 4'-diphenyl dicarboxylic acid, - diphenyl ether dicarboxylic acid, and 3 and 3 '3, 4'-diphenyl ether dicarboxylic acid, 4 and 4'-diphenyl ether dicarboxylic acid, 2, and 2-screw (4-carboxyphenyl) hexafluoropropane, - benzophenone dicarboxylic acid, and 3 and 3 '3, 4'-

benzophenone dicarboxylic acid, - diphenyl sulfone dicarboxylic acid, and - benzophenone dicarboxylic acid, and 4 and 4 '3, 3'-diphenyl sulfone dicarboxylic acid, 3, and 4 '4, 4'-diphenyl sulfone dicarboxylic acid etc. is mentioned. Moreover, even if these are independently used in an activity, it does not matter even if it is two or more sorts of concomitant use.

[0012] On the other hand as dihydroxy diamine used for the polyamide manufacture before esterification For example, 2, a 4-dihydroxy-m-phenylenediamine, 2, 5-dihydroxy-p-phenylene diamine, 4, 6-diamino resorcinol, 3, the 3'-diamino -4, 4'-dihydroxydiphenyl, 4 and 4' -- the - diamino -3 and 3' - dihydroxydiphenyl, and 3 and 4 -- 'the - diamino -3' and 4-dihydroxydiphenyl -- 3, the 3'-diamino -4, 4'-dihydroxy diphenyl ether, 4, the 4'-diamino -3, 3'-dihydroxy diphenyl ether, 3, 4'-diamino - 3', 4'-dihydroxy diphenyl ether, 3, the 3'-diamino -4, 4'-dihydroxydiphenyl hexafluoropropane, 4, the 4'-diamino -3, 3'-dihydroxydiphenyl hexafluoropropane, 3, 4'-diamino - 3', 4-dihydroxydiphenyl hexafluoropropane, 3, the 3'-diamino -4, a 4'-dihydroxy benzophenone, 4, the 4'-diamino -3, a 3'-dihydroxy benzophenone, 3 4'-diamino - 3', 4-dihydroxy benzophenone, 3, the 3'-diamino -4, 4'-dihydroxydiphenyl sulfone, 4 and 4' -- the - diamino -3 and 3' - dihydroxydiphenyl sulfone, and 3 and 4 -- 'the - diamino -3', 4-dihydroxydiphenyl sulfone, etc. are mentioned. Moreover, in an activity, even if these may be independent and are two or more sorts of concomitant use, they are not cared about.

[0013] At this time, it can also consider as aromatic series or silicone diamine without a phenol nature OH radical in the range which does not exceed 40-mol% of all diamines for a part of dihydroxy diamine. As diamine without a phenol nature OH radical For example, m-phenylenediamine, p-phenylene diamine, 2, 5-diaminotoluene, 3, 5-diaminotoluene, 2, 4-diaminotoluene, meta xylene -2, 5-diamine, Para xylene -2, 5-diamine, 2, 6-diamino pyridine, 2, 5-diamino pyridine, 2, 5-diamino - 1, 3, 4-OKISA diazole, 1, 4-diamino cyclohexane, A piperazine, methylene diamine, ethylenediamine, propylenediamine, 2 and 2-dimethyl propylenediamine, a tetramethylenediamine, pentamethylene diamine, A hexamethylenediamine, 2, 5-dimethyl hexamethylenediamine, 3-methoxy hexamethylenediamine, heptamethylene diamine, 2, 5-dimethyl heptamethylene diamine, A 3-methyl heptamethylene diamine, 4, and 4'-diamino diphenyl propane, - diamino diphenyl propane, and 3 and 3 '4, 4'-diamino bibenzyl, - diamino bibenzyl, and 3 and 3 '4, 4'-diamino diphenylmethane, A - diamino diphenylmethane, and 3 and 3 '4, 4'-diamino diphenyl sulfide, - diamino diphenyl sulfide, and 3 and 3 '4, 4'-diamino diphenyl sulfone, - diamino diphenyl sulfone, and 3 and 3 '4, 4'-diamino diphenyl ether, - diamino diphenyl ether, and 4 '3, 3'-diamino diphenyl ether, [ 3, and ] The 3 and 3'-dimethyl -4, a - diamino biphenyl, and 4 '3, 3'-dimethoxy benzidine, - diamino-para terphenyl, and 4 and 4 '3, 3'-diamino-para terphenyl, Screw (p-amino cyclohexyl) methane, the screw (p-beta-amino-t-buthylphenyl) ether, Screw (p-beta-methyl-delta-amino pentyl) benzene, p-screw (2-methyl-4-amino pentyl) benzene, p-screw (1 and 1-dimethyl-5-amino pentyl) benzene, 1, 5-diamino naphthalene, 2, 6-diamino naphthalene, 1, 3-screw (3-amino phenoxy) benzene, 1, 4-screw (4-amino phenoxy) benzene, 1, 3-screw (gamma-aminopropyl) tetramethyl disiloxane, 1, 3-screw (p-aminophenyl) tetramethyl disiloxane, 1, 4-screw (gamma-aminopropyl dimethylsilyl) benzene, 1, 3-screw (4-amino butyl) tetramethyl disiloxane, 1, 3-screw (gamma-aminopropyl) tetra-phenyl disiloxane, 1, 3-screw (4-amino phenoxy) tetramethyl disiloxane, 1, 3-screw (3-amino phenoxy) tetramethyl disiloxane, 4 and 4' - screw (4-amino phenoxy) biphenyl and screw [4-(4-amino phenoxy) phenyl] ether, Screw [4-(3-amino phenoxy) phenyl] sulfone, screw [4-(4-amino phenoxy) phenyl] sulfone, 4 and 4'-screw [4-(4-amino phenoxy) phenoxy] diphenyl sulfone, - screw (3-amino phenoxy) biphenyl, and 4 and 4 '2, 2' screw [ - ] [4-(4-amino phenoxy) phenyl] propane, 2 and 2' screw [ - ] [4-(4-amino phenoxy) phenyl] hexafluoropropane, 2 and 2' screw [ - ] [4-(3-amino phenoxy) phenyl] hexafluoropropane, Although - diamino -3, 3', and 4 and 4 '5, 5'-tetramethyl diphenylmethane, 2, and 6-diamino-4-carboxy rucksack benzene (methacrylic-acid-2-hydroxyethyl) ester etc. is mentioned, it is not limited to these. Moreover, in an activity, even if these may be independent and are two or more sorts of concomitant use, they are not cared about. If the mole ratio of the diamine which does not have a phenol nature OH radical among all diamines exceeds 40%, since the compatibility over the alkaline developer of the polyamide of this invention falls remarkably and development becomes impossible substantially, it is not desirable.

[0014] Moreover, as an example of the acid anhydride which can be used in order to close a chain end, a

maleic anhydride, the cis-4-cyclohexene -1, 2-dicarboxylic acid anhydride, 5-norbornene -2, 3-dicarboxylic acid anhydride, methyl-5-norbornene -2, 3-dicarboxylic acid anhydride, etc. are mentioned. On the other hand, as an example of acid chloride, benzoyl chloride, methane sulfonyl chloride, p-toluene sulfonyl chloride, etc. are mentioned. However, what can be used in order to close a molecule end in the case of manufacture of the polyamide of this invention is not limited to this.

[0015] Although the photosensitive polyamide in this invention is manufactured according to esterification of the polyamide by 1, 2-naphthoquinonediazide-4-sulfonic acid, 1, and 2-naphthoquinonediazide-5-sulfonic acid and those acid halide, 1 - 50% of the rate of esterification is desirable to the hydrogen atom of the hydroxyl group in the polyamide before esterification, and is more desirable. [ further 3 - 20% of ] At less than 3%, when the dissolution suppression effect as opposed to a photopolymer constituent in the rate of esterification is small, buildup of the unexposed \*\*\*\* decrease by the lack of contrast may be seen and 20% is exceeded on the other hand, the development remainder may arise into an exposure portion. Acid halide, such as 1, 2-naphthoquinonediazide-4-sulfonic acid, 1, and 2-naphthoquinonediazide-5-sulfonic acid or it, may be used independently, respectively, and may use two sorts together. In the photopolymer constituent of this invention, a photosensitive polyamide has that desirable whose weight average molecular weight is 5,000 to about 50,000.

[0016] It is also possible to add the sensitization material as the adhesion assistant for raising adhesion with the color and surfactant which are conventionally used as an additive of a photopolymer constituent if needed, a stabilizer, a dissolution accelerator, and a substrate to the photopolymer constituent of this invention, and a contrast enhancement agent etc.

[0017] When the above-mentioned additive is described still more concretely, as a color Methyl Violet, a crystal violet, Malachite Green, etc. for example, as a surfactant For example, the non-ion system surfactant which consists of polyglycols, such as a polypropylene glycol or the polyoxyethylene lauryl ether, or a derivative of those, for example, Fluorad (a trade name, Sumitomo 3 M company make) and a megger fuck (a trade name --) Fluorochemical surfactants, such as the Dainippon Ink & Chemicals, Inc. make or SURUFURON (a trade name, Asahi Glass Co., Ltd. make), Organic siloxane surfactants, such as KP341 (a trade name, Shin-Etsu Chemical Co., Ltd. make), for example, as an adhesion assistant For example, various and silane coupling agents, such as alkyl imidazoline, butanoic acid, an alkyl acid, polyhydroxy styrene, polyvinyl methyl ether, t-butyl novolak, an epoxy silane, and epoxy polymer, are mentioned.

[0018] Moreover, as a dissolution accelerator, the compound which has a phenolic hydroxyl group is desirable, for example, non-straight chain-like phenolic compounds (all Honshu Chemical Industry Co., Ltd. make), such as straight chain-like phenolic compounds, such as a bisphenol or MtrisPC, and MtetraPC, TrisP-HAP, TrisP-PHBA, and TrisP-PA, are mentioned. Furthermore, as sensitization material, an ester reaction compound with trihydroxy benzophenone, tetra-hydroxy benzophenone, TrisP-HAP, TrisP-PHBA, TrisP-PA, etc. 1 and 2-naphthoquinonediazide-4-sulfonyl chloride or 1, and 2-naphthoquinonediazide-5-sulfonyl chloride etc. is mentioned.

[0019] In this invention, these components are dissolved in a solvent, and it is made the shape of a varnish, and is used as a photopolymer constituent. As a solvent, a N-methyl-2-pyrrolidone, gamma-butyrolactone, N,N-dimethylacetamide, dimethyl sulfoxide, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dibutyl ether, Propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, Propylene-glycol-monomethyl-ether acetate, methyl lactate, independent in ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. -- or it can be mixed and used.

[0020] The developer used in order to develop the photopolymer film formed with the photopolymer constituent of this invention needs to be the alkali aqueous solution which carries out dissolution clearance of the alkali fusibility polymer, and dissolved the alkali compound. The alkali compounds dissolved into a developer may be any of an inorganic alkali compound and an organic alkali compound. As an inorganic alkali compound, a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, diammonium hydrogenphosphate, the potassium phosphate, disodium hydrogenphosphate, ammonium

dihydrogenphosphate, a potassium dihydrogenphosphate, a sodium dihydrogenphosphate, a silicic-acid lithium, a sodium silicate, a potassium silicate, a lithium carbonate, a sodium carbonate, potassium carbonate, lithium borate, the sodium borate, a boric-acid potassium, ammonia, etc. are mentioned, for example. Moreover, as an organic alkali compound, tetramethylammonium hydroxide, trimethylhydroxyethylammonium hydroxide, monomethylamine, dimethylamine, a trimethylamine, a monoethyl amine, diethylamine, triethylamine, mono-isopropylamine, diisopropylamine, ethanolamine, etc. are mentioned, for example. Furthermore, optimum dose addition of water-soluble organic solvents, such as a methanol, ethanol, propanol, and ethylene glycol, a surfactant, a conservation stabilizer, the dissolution retardant of resin, etc. can be carried out at the above-mentioned alkali aqueous solution if needed.

[0021] The photopolymer constituent of this invention can be used as follows. First, a photopolymer constituent is applied by revolution spreading and the roll coater which used the spinner for the suitable substrate, for example, a silicon wafer, the ceramic substrate, the aluminum substrate, etc. This is dried at 50-140 degrees C using oven or a hot plate, and chemical rays are irradiated through a mask using a contact aligner or a stepper. Next, dissolution clearance of the exposure section is carried out with a developer, and a desired relief pattern is obtained by performing the rinse by the rinse succeeding. As the development method, methods, such as a spray, a paddle, a DIP, and an ultrasonic wave, are possible. A rinse can use distilled water, deionized water, etc. The obtained relief pattern can be heat-treated and the heat-resistant coat which has oxazole structure can be formed. The photopolymer constituent by this invention is useful also as the layer insulation of not only a semiconductor use but a multilayer circuit, the cover coat of a flexible copper-clad sheet, a solder resist film, a liquid crystal orientation film, etc.

[0022]

[Embodiment of the Invention] Although the example of reference (synthetic example of a polyamide), an example, and the example of a comparison are given and this invention is explained still more concretely hereafter, of course, the gestalt of operation of this invention is not what is limited to these examples shown concretely.

[0023] The example 1 (composition 1 of a polyamide) of reference

In the 4 and 4'-diphenyl ether dicarboxylic acid (69 0.27 mols, 7g) taught to 3L separable flask which attached the agitator, the dropping funnel, and the thermometer, and the N,N-dimethylacetamide (600g) solution of N and N-dimethylamino pyridine (0.03 mols, 3.7g), at a room temperature, a thionyl chloride (0.63 mols, 75.0g) is dropped, and it stirs for 1 hour. This solution is added to 3, the 3'-diamino -4, and the N,N-dimethylacetamide (300g) solution of 4'-dihydroxydiphenyl hexafluoropropane (0.30 mols, 109.9g) which were put into 3L separable flask at 0 degree C, and is stirred under a room temperature for 6 hours. 5-norbornene -2 and 3-dicarboxylic acid anhydride (9 0.06 mols, 8g) were added to this solution, it stirred for further 10 hours, and acid closure of the chain end was carried out. This was diluted with N,N-dimethylacetamide (1000g), and it was dropped, stirring in water, water was removed, the vacuum drying was carried out at 40 degrees C, and the polyamide (P-1) was obtained.

[0024] The examples 2 and 3 (composition 2 and 3 of a polyamide) of reference

considering as the compound and the amount used which show dicarboxylic acid, diamine, and end encapsulant in the following table 1 -- removing -- the example 1 of reference -- the same -- carrying out -- a polyamide (P-2) -- and (P-3) it compounded.

[0025]

[A table 1]



参考例	ポリアミド No.	ジカルボン酸	ジアミン	末端封止剤
1	P-1	4,4'-ジフェニルエーテル ジカルボン酸 0.27mol, 69.7g	3,3'-ジアミノ-4,4'- ジヒドロキシフェニル チオエーテル 0.30mol, 109.9g	5-ナフチル-2,3-ジ カルボン酸無水物 0.06mol, 9.8g
2	P-2	イソフタル酸 0.135mol, 22.4g テレフタル酸 0.135mol, 22.4g	3,3'-ジアミノ-4,4'- ジヒドロキシフェニル チオエーテル 0.30mol, 109.9g	5-ナフチル-2,3-ジ カルボン酸無水物 0.06mol, 9.8g
3	P-3	4,4'-ジフェニルエーテル ジカルボン酸 0.27mol, 69.7g	3,3'-ジアミノ-4,4'- ジヒドロキシフェニル チオエーテル 0.30mol, 109.9g	無水フタル酸 0.06mol, 8.9g

[0026] Example 1 (composition 1 of a photosensitive polyamide)

1 and 2-naphthoquinonediazide-4-sulfonic acid chloride and acetone 390g of the amount equivalent to above-mentioned polyamide (P-1) 80g and eight-mol% of the OH radical of this polyamide was taught to 1L separable flask which attached the agitator, the dropping funnel, and the thermometer, and after carrying out stirring dissolution, the thermostat adjusted the flask at 30 degrees C. Next, after dissolving triethylamine 3g in acetone 12g and teaching a dropping funnel, this was dropped into the flask over 30 minutes. Stirring was continued for 30 more minutes after dropping termination, the hydrochloric acid was dropped after that, stirring was performed for 30 more minutes, and the reaction was terminated. It filtered after that and the triethylamine hydrochloride was removed. It was dropped stirring the filtrate obtained here to 3L beaker which carried out mixed stirring of 2000g of pure water, and the 27g of the hydrochloric acids, and the sludge was obtained. After rinsing and filtering this sludge, it dried under 40 degrees C and reduced pressure for 48 hours, and the photosensitive polyamide (A-1) was obtained.

[0027] Thus, when the molecular weight of the compounded photosensitive polyamide (A-1) was measured also as that of the following conditions with gel permeation chromatography (GPC), the weight average molecular weight was 12,000 in polystyrene conversion.

(Determination-of-molecular-weight conditions of a photosensitive polyamide)

GPC column: KF-804 1, KF-802 2 and KF-801 One (all are the Showa Denko K.K. make)

Rate of flow: 1.0 ml/min column temperature: 40-degree-C mobile phase: THF for liquid chromatography [0028] Examples 2-5 (composition 2-5 of a photosensitive polyamide)

As a polyamide and naphthoquinonediazide sulfonic acid chloride, photosensitive polyamide (A-2) - (A-5) was compounded like the example 1 except for changing the amount used to the polyamide of the naphthoquinonediazide sulfonic acid chloride to be used, and considering as the rate of esterification of a table 2, using the compound respectively shown in a table 2. When the compounded photosensitive polyamide (A-2) - (A-5) molecular weight (polystyrene equivalent weight average molecular weight) were measured by the same method as an example 1, for A-2, as for 12,000 and A-4, 12,000 and A-3 were [ 12,000 and A-5 ] 10,500.

[0029] The example 4 (composition 6 of a photosensitive polyamide) of reference

Except for using (P-3) as a polyamide, the photosensitive polyamide (A-6) was compounded like the example 1. It was 10,000 when the molecular weight (polystyrene equivalent weight average molecular weight) of the compounded photosensitive polyamide (A-6) was measured by the same method as an example 1.

[0030]

[A table 2]

	感光性ポリアミド No.	ナフトキノンジアジド スルホン酸クロライド	ポリアミド	エステル化率
実施例 1	A-1	1, 2-ナフトキノンジアジド-4-スルホン酸クロライド	P-1	8%
実施例 2	A-2	1, 2-ナフトキノンジアジド-4-スルホン酸クロライド	P-1	7%
実施例 3	A-3	1, 2-ナフトキノンジアジド-4-スルホン酸クロライド	P-1	6%
実施例 4	A-4	1, 2-ナフトキノンジアジド-5-スルホン酸クロライド	P-1	8%
実施例 5	A-5	1, 2-ナフトキノンジアジド-4-スルホン酸クロライド	P-2	8%
参考例 4	A-6	1, 2-ナフトキノンジアジド-4-スルホン酸クロライド	P-3	8%

[0031] After dissolving the photosensitive polyamide (A-1) 100 weight section obtained in the example 6 example 1 in the gamma-butyrolactone 230 weight section, it filtered with the 0.5-micrometer Teflon (registered trademark) filter, and the photopolymer constituent was prepared. Spin spreading of this constituent was carried out in the spin coater (LARC ULTIMA-1000) by Litho Tech Japan Corp. at the 6 inch silicon wafer, for 130 degrees C and 180 seconds, it prebaked with the hot plate and the 13-micrometer paint film was formed. Thickness was measured with the Dainippon Screen Mfg. Co., Ltd. film production thickness measuring device (lambda ace). Using the stepper (the NIKON make, NSR1755i7B) which has the exposure wavelength of i-line (365nm) through reticle with a test pattern in this paint film, light exposure was changed gradually and exposed. Negatives were developed by having adjusted developing time so that the thickness after development might be set to 10.5 micrometers under 23-degree C conditions using the Clariant Japan alkali developer (an AZ300MIF developer and 2.38 % of the weight tetramethylammonium hydroxide aqueous solution; AZ are a registered trademark) in this, and the positive pattern was formed. The sensitivity of developing time and a photopolymer constituent, the existence of Society for Cutting Up Men of the obtained pattern, and a pattern configuration are shown in a table 3.

[0032] In addition, the sensitivity of a photopolymer constituent, the existence of Society for Cutting Up Men, and a pattern configuration were determined or observed as follows.

The minimum light exposure which a line and a space with a sensitivity of 50 micrometers or more resolve.

The existence of the residue between the lines of a Society for Cutting Up Men 10micrometer line and a space is observed with an optical microscope.

The cross-section configuration of pattern configuration the line of 10 micrometers and, and a space is observed with an electron microscope.

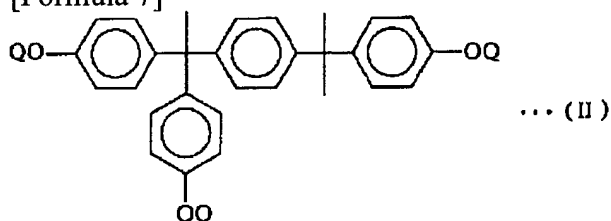
[0033] Except for considering as the photosensitive polyamide which shows an example 7 - 10 photosensitivity polyamide in a table 3, the photopolymer constituent was prepared like the example 6, and it processed by the same actuation as an example 6. Assessment (the existence and the pattern configuration of the sensitivity of developing time and a photopolymer constituent and Society for Cutting Up Men of the obtained pattern) about the photopolymer constituent of each example was performed like the example 6. A result is shown in a table 3.

[0034] It replaced with the example of comparison 1 photosensitivity polyamide (A-1), the photopolymer constituent was prepared like the example 6 except for using the photosensitive polyamide (A-6) which is not contained in the photosensitive polyamide of this invention and which was manufactured using the polyamide (P-3), and it processed by the same actuation as an example 6. Assessment about this photopolymer constituent was performed like the example 6. A result is shown in a table 3.

[0035] After dissolving the example of comparison 2 polyamide (P-1) 100 weight section, and the sensitization material 15 weight section shown by the following formula (II) in the gamma-butyrolactone 230 weight section, it filtered with the 0.5-micrometer Teflon filter, the photopolymer constituent was prepared, and it processed by the same actuation as an example 6. Assessment about this photopolymer constituent was performed like the example 6. A result is shown in a table 3.

[0036]

[Formula 7]



Q:90% is 1 and 2-naphthoquinonediazide-4-sulfonic acid residue, and 10% is a hydrogen atom.

[0037]

[A table 3]

	感光性ポリアミド	現像時間 [sec]	感度 [mJ/cm <sup>2</sup> ]	スカム	パターン形状
実施例 6	A-1	102	300	なし	良好
実施例 7	A-2	86	350	なし	良好
実施例 8	A-3	68	375	なし	良好
実施例 9	A-4	88	525	なし	良好
実施例 10	A-5	78	425	なし	良好
比較例 1	A-6	42	>900	なし	細り
比較例 2	P-1 + 式 (II) の感光材	70	375	なし	細り

[0038] A table 3 shows that there is no Society for Cutting Up Men, and a polyamide pattern with a good pattern configuration can be formed by high sensitivity by using the photopolymer constituent of this invention. Moreover, the heat-resistant coat the pattern obtained in the examples 6-10 all excelled [coat] in the mechanical property with heating was formed.

[0039]

[Effect of the Invention] As explained in full detail above, according to this invention, it is high sensitivity, a high remaining rate of membrane, and high contrast, and the photopolymer constituent which was especially excellent in the pattern configuration after development and the definition of a detailed pattern can be obtained. The photopolymer constituent of this invention is a suitable material for formation of surface-protection films, such as a semiconductor device, an interlayer insulation film, etc.

[Translation done.]